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C5E ECC E232 E355 E381 E384
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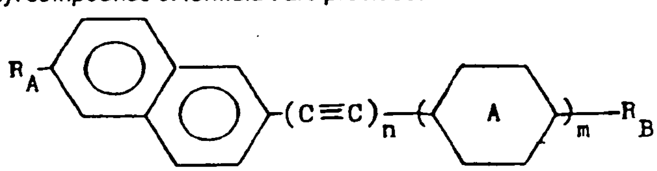
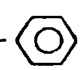
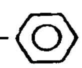
(54) Naphthyl compounds and their use in liquid crystal materials and devices

(57) Novel naphthyl compounds of formula I are provided:



formula I

wherein R_A is independently selected from R, RO, R-C≡C–, R–  –C≡C– and RO–  –C≡C– where R is C_1–C_{12} alkyl or perfluoroalkyl;
wherein n is 0 or 1, m is 0 or 1;
wherein ring A is phenyl, monofluorophenyl, difluorophenyl or *trans* cyclohexyl; and
wherein R_B is independently selected from R¹, OR¹, –C≡CR¹, –CN or –C≡CN where R¹ is C_1–C_{12} alkyl or perfluoroalkyl; *provided* that the compound of Formula 1 contains at least one C≡C group and further *provided* that if n is 1 and m is 0 th n R_B is not OR¹, C≡CR¹, or C≡CCN.

These compounds have nematic liquid crystalline properties and are suitable for use as ingredients of liquid crystal materials for use in electro-optic devices.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

NAPHTHYL COMPOUNDS AND THEIR USE IN LIQUID CRYSTAL MATERIALS AND DEVICES.

This invention relates to naphthyl compounds, in particular those which show liquid crystalline phases of a type which are suitable for use in liquid crystal electro-optic display devices. The invention also relates to liquid crystalline materials which are mixtures containing these naphthyl compounds, and to display devices which use them.

Liquid crystal electro-optic display devices use liquid crystalline materials of two general types. There are those which show a nematic or cholesteric (N, Ch) phase, and those which show a smectic (S) phase, of which the most widely used is the ferroelectric chiral smectic C phase (S_c^*). Other smectic phases which are useful in electro-optical display devices are the smectic A and I phases (SA, SI).

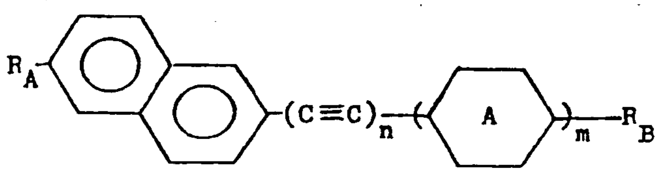
For use in such devices it is desirable that a compound or a material containing it shows liquid crystal phases of the desired type which includes the intended working temperature range of the device (generally at least 0-60°C), has a low viscosity, is stable and easy to prepare, and has useful physico-chemical properties such as birefringence, dielectric anisotropy etc.

In the case of S_c^* compounds and materials it is also desirable that the compound or material shows the phase transition sequence $S_c^* \rightarrow S_A$ on increasing temperature to assist alignment of the material within the device. Further desirable requirements of an S_c^* compound or material are a high spontaneous polarisation (Ps), and a long helical pitch in the S_c^* phase.

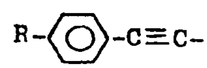
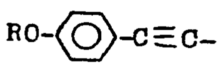
It is rare that all of these requirements are found in a single compound, so it is usual to use a mixture of compounds, containing one or more compounds which either separately or together show a useful liquid crystal phase. In the case of S_c^* mixtures, such a mixture generally contains one or more compounds which separately or together show an Sc phase (known as "hosts") plus one or more optically active compounds (known as "dopants"), ie which contain an asymmetrically substituted carbon atom, the function of th optically active compound being to induce chirality into the mixture.

It is an object of the invention to provide compounds which can be used as components of such mixtures, particularly as components of high birefringence nematic mixtures.

According to the invention, there are provided novel napthyl compounds of Formua 1:



formula I

wherein R_A is independently selected from R, RO, R-C≡C-,  and  where R is C_1-C_{12} alkyl or perfluoroalkyl;

wherein n is 0 or 1, m is 0 or 1;
wherein ring A is phenyl, monofluorophenyl, difluorophenyl or <u>trans</u> cyclohexyl; and
wherein R_B is indepently selected from R^1, OR^1, $-C{\equiv}CR^1$, -CN or -C≡C-CN where R^1 is C_1-C_{12} alkyl or perfluoroalkyl;
<u>provided</u> that the compound of Formula 1 contains at least one C≡C group and further <u>provided</u> that if n is 1 and m is 0 then R_B is not OR^1, $C{\equiv}CR^1$, or C≡CCN.

The structural preferences discussed below are inter alia on the basis of ease of preparation or usefulness in liquid crystal mixtures.

Preferably R and R^1 are straight chain alkyl.

Preferred compounds of Formula I are therefore the cases in which either:

$n = 1$ and $m = 0$, R_A is R or RO, and R_B is -CN or R^1; <u>or</u>

$n = 0$ and $m = 0$, R_A is R-C C-, R_B is CN; <u>or</u>

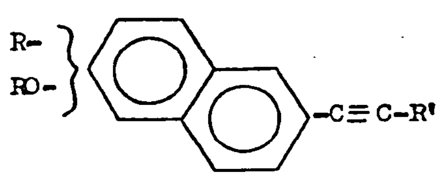
$n = 1$ and $m = 1$, R_A is R-, RO- or R-C C, R_B is R^1, OR^1, $-C{\equiv}CR^1$, -CN or -C≡CCN and ring A is phenyl, monofluorophenyl or difluorophenyl.

When R_A or R_B is or contains an alkyl group, it may be n-alkyl, branched alkyl or asymmetrically substituted alkyl. R_A and R_B preferably contain 3-10 carbon atoms and are perferably straight chain when they are other than CN or -C≡C-CN.

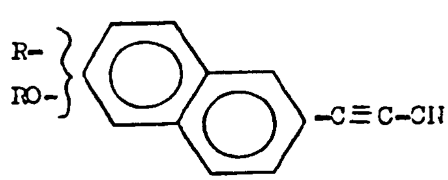
When ring A is monifluorophenyl or difluorophenyl the fluorine substituents(s) may be in any of the available substitution positions. Preferably if ring A is monofluorophenyl the fluorine is in the 3 positions adjacent to R_B.

Preferred overall structures for compounds of Formula I are therefore listed below in Table 1.

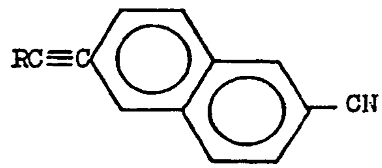
<u>Table 1</u>



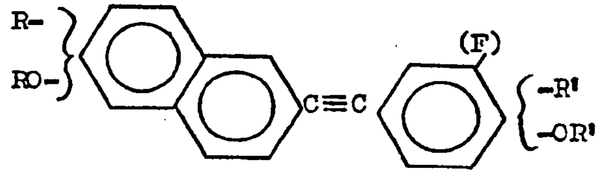
IA



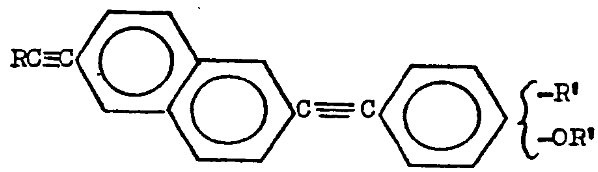
IB



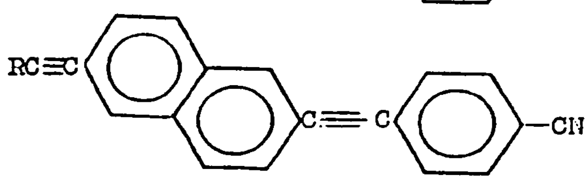
IC



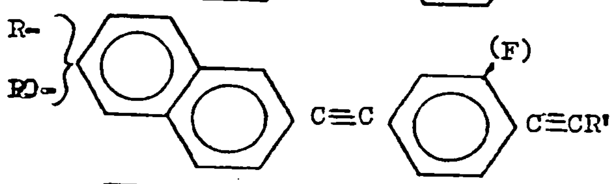
ID



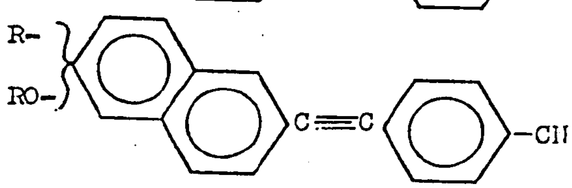
IE



IF



IG



IH

In Formula IA, IB, ID, IC and IH above it is particularly preferred that R_A is RO-, especially $C_6 - C_{10}$ n-alkoxy. In Formula ID R_A is preferably n-alkoxy and R_B n-alkyl. (F) indicates that there may be a fluorine subsitituent in the indicated ring position.

Compounds of Formulae IA to IH above may be prepared by preparative routes shown schematically in Figure 1, where for example Route A leads to compounds of Formula IA etc, and steps P1 and P2 are preliminary steps to intermediates.

The individual steps used in these routes are known, albeit in some cases with analogous or homologous compounds.

Step P1 RBr, K_2CO_3, acetone solvent (or when R = methyl, dimethyl sulphate, KOH.

Step P2 CuI, KI, hexamethylphosphoramide (HMPA)

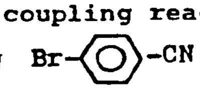
Route A Zinc Chloride, lithium acetylide ethylene diamine complex. Couple with tetrakis (triphenyl phosphine) palladium(O) ("TTPP").

Route B (B1) Bromine, or N-Bromosuccinimide
(B3) CuCN, Dimethylformamide ("DMF")

Route C (C1) CuCN, DMF
(C2) BBr_3/CH_2Cl_2 or $AlCl_3$/NaCl
(C3) N-phenyltrifluoromethane sulphonimide ("NPTFMS") dichloromethane
(C4) RC≡CH, n- BuLi, $ZnCl_2$, TTPP, THF solvent

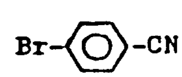
Route D (B1) as Step P1
(D2) as Route B
(D3) diazotisation, KI
(D4) as Route B
(D5) as Route B

Route E (EI) BBr_3
(E2) NPTFMS
(E3) nBuLi, TTPP, LiCl
(E4) nBuli, $ZnCl_2$, TTPP, LiCL

Route F (F1) coupling reaction as in Step A1
using 
(F2) as Step C2
(F3 - F4) as steps C3 and C4

Route G (G1) (i) R^1C CH, nBuLi, THF
(ii) $ZnCl_2$
(iii) couple as Step C4

(G2) couple as in Step B

Route H (H1) as Route A, couple with 

Suitable reaction conditions for these steps will be apparent to those skilled in the art. Variations of these routes can be used to form other compounds of Formula I.

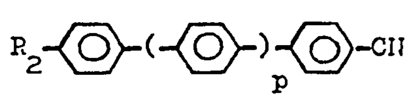
Also by starting from the known 2-alkyl-6-bromo naphthalene instead of the 2-alkoxy product of Step P1, the corresponding compounds where R_A is alkyl may in many cases be prepared, for example in Routes A, D, B, H and I at least.

The invention also provides a liquid crystal material, being a mixture of compounds which shows a liquid crystal phase, at least one of the compounds being a compound of Formula I. The liquid crystal phase is preferably an N or S_C phase.

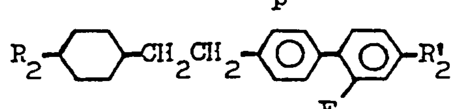
Preferred compounds of Formula I for such a mixture are those discussed above. Compounds of structures encompassed by Formula I are suitable for N mixtures for example compounds of structure ID show N phases with high clearing points. For use in Sc and Sc mixtures preferred compounds of Formula I are those in which ring A is difluorophenyl, especially 2, 3 -difluorophenyl, R_A and R_B being especially alkyl or alkoxy.

When used as components of nematic mixtures, compounds of Formula I or mixtures thereof may on occasions be used by themselves, but they will normally be used as additives together with a major proportion of other compounds which either separately or when mixed show a nematic phase.

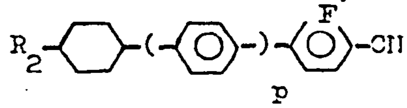
A large variety of such suitable nematic compounds are well known but it is particularly preferred that the mixture contains compounds of Formula II:



IIA



IIB



IIC

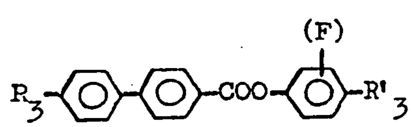
where R_2 and $R^1{}_2$ are C_1-10 n-alkyl or n-alkoxy and p is 0 or 1.

For example a typical nematic mixture of this aspect of the invention may contain 1-95%, preferably 50-95% by weight of compounds of Formula II, especially of Formula IIA in which p is 0. It may also include up to about 25% of compounds of Formula IIA in which p is 1 to increase the N-I transition temperature and/or may contain or comprise one or more compounds at Formula IIB which can lower the melting point.

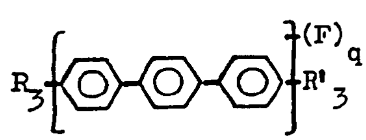
Compounds of Formula I which contain one or more C≡C groups are expected to have a high birefringence, which is of particular value for use in liquid crystal materials intended for devices which exploit the electrically controlled birefringence effect (ECB effect). Devices of this type are known.

Compounds of Formula I and/or mixtures thereof may be suitable by themselves for use as Sc hosts or described above but more commonly they may be used as a component of a host mixture together with one or more known Sc host compounds, optionally together with additives which improve the properties of the mixture, or modify if for some particular application.

Particularly preferred hosts are the known compounds of Formulae III:



IIIA

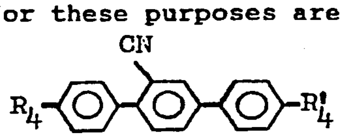


IIIB

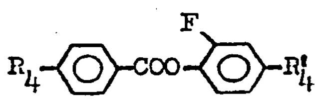
where R_3 and R^1 are independently C_3 - C_{12} n-alkyl or n-alkoxy and q in Formula IIIB is 1 or 2. In Formula IIIA the fluorine substituent is preferably adjacent to the ester linkage. In Formula IIIB where q is 1 the fluorine is preferably on the central ring and

when q is 2 the fluorines are preferably in the 2, 3 - or 2^1, 3^1 - positions.

Additives may for example include compounds which suppress undesirable smectic phases such as S_B, or which promote the phase transition sequence S_C - S_A at higher temperatures. Examples of additives which may be used for these purposes are compounds of Formula IV



IVA

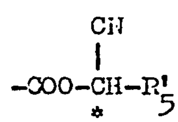


IVB

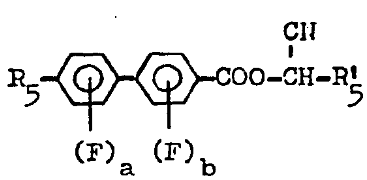
wherein R_4 and $R^1{}_4$ are independently C_1 - C_{12} n-alkyl or n-alkoxy.

When the mixture is intended to shown an Sc phase it is necessary to include one or more optically active dopants in the mixture. A large variety of such dopants is known, for example, the compounds described in EP-A-0110299.

Particularly preferred dopants are, however, the compounds containing an asymmetrically substituted group:

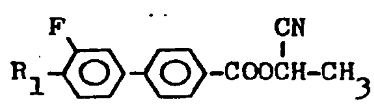


where R_5' is C_1 - C_8 alkyl, especially C_1 - C_4 n-alkyl or a branched alkyl group. Particularly preferred groups R_3 are methyl or $Ch(CH_3)_2$. In these preferred dopants this group is linked to a mesogenic core, in particular in compounds such as:

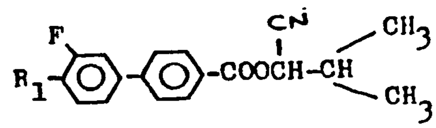


V

where a and b are independently 0 or 1, (a + b) being 0 or 1, R_5 being C_{1-12} n-alkyl or alkoxy. These compounds and related dopants containing this asymmetrically substituted group are described for example in WO87/07890 and PCT/GB 88/01111. Particularly preferred compounds of Formulae V are:



VA



VB

It is generally preferred that at least 2 dopants are included, having opposite twisting effects on the Sc phase, to promote a long helical pitch in the Sc* phase, to promote a long helical pitch in the Sc* phase.

In an Sc host mixture of this aspect of the invention the proportion in weight % of these various components is generally as below:

Host compound(s)	0-99 (preferably 80-99)
Compound(s) of Formula I	1-99 (preferably 1-20)
Additive(s)	0-20
Total	100

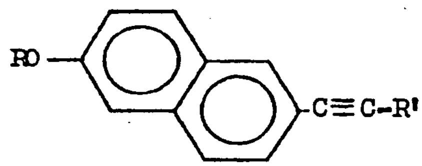
An Sc* mixture will additionally also contain 1-20 weight % of dopant(s).

Liquid crystal materials of this invention may be used in any of the known types of liquid crystal electro-optical display device which exploit electro-optical effects manifested by the nematic or smectic liquid crystal phases. The construction and operation of such devices is well known.

The invention will now be describ d by way of example only with reference to the accompanying figures, which show:

Fig 1	Preparative Routes A, D, E, G, H.
Fig 2	Preparative Routes B, C, F.

Example 1 Preparation of Type IA Compounds



2 - Bromo-6-Methoxynaphthalene

Step P1. Dimethylsulphate (33.8g, 0.268 mol) was added to a stirred solution of 2-hydroxy-6-bromonaphthalene (50 g, 0.224 mol) and potassium hydroxide (15g, 0.268 mol) in water (220 ml) at room temperature. The stirred mixture was heated at 70°C for 1 hour and stirred overnight at room temperature (tlc and glc revealed a complete reaction). The product was filtered off, washed with 10% sodium hydroxide then water, then dried well and extracted into dichloromethane. The organic extract was washed with 10% sodium hydroxide, water and then dried (Mg SO_4). The solvent was removed *in vacuo* to give a colourless solid. *Yield* 50.9g (96%) mp 108-110°C.

Step P1 2-Bromo-6-alkoxy naphthalene A solution of 1-bromobutane (50g, 0.36 mol) in acetone (30 ml) was added dropwise to a stirred refluxing mixture of 2-hydroxy-6-bromonaphthalene (40g 0.18 mol) and potassium carbonate (51g 0.37 mol) in acetone (300 ml). The stirred mixture was heated under reflux for 24 hours (tlc and glc revealed a complete reaction). The potassium carbonate was filtered off, water and dried (Mg SO_4). The solvent and the excess of 1-bromobutane were removed *in vacuo*. The product was recrystallised from etharol to yield an off-white powder. *Yield* 32.2g (64%) mp 52-53°C.

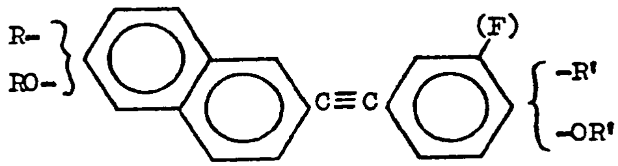
Step P2 - 2-Iodo-6-Alkoxy Naphthalenes. A mixture of 2-bromo-6-methoxy naphthalene from Step P1 (15g, 0.063 mol), potassium iodide (158g, 0.95 mol) and copper(I) iodide (60.5, 0.32 mol) in hexamethyl phosphoramide (HMPA) (180 m l) was stirred at 160°C under dry nitrogen for 18 hours (glc analysis revealed complete reaction). The cooled mixture was poured into 10% hydrochloric acid (300 ml) and the product was extracted into ether and left overnight at room temperature. Insoluble copper salts were filtered off and washed well with ether and the separated aqueous layer was washed with ether. The combined ethereal extracts were washed with water, aqueous sodium sulphite, water and dried (Mg SO4). The solvent was removed *in vacuo* to yield a pale yellow solid. Yield 17.50g (78%) mp 138-140°C.

This procedure was repeated using 2-iodo-6-butoxy naphthalene from Step P1 (20g 0.072 mol), potassium iodide (180g 1.08 mol), copper(I) iodide (68.6g 0.36 mol) HMPA (220 ml). Yield 22.75 g(97%) mp 66-67°C.

Route A - 6-Methoxynaphth-2-ylethyne. A solution of zinc chloride (13.5g, 0.098 mol) in dry THF (100 ml) was added dropwise to a stirred, cooled (-5 to 0°C) solution of lithium acetylide ethylene-diamine complex (9.0g 0.098 mol) in dry THF (100 ml) under dry nitrogen. The mixture was stirred at 10°C for 30 minutes and a solution of 1-iodo-6-methoxy naphthalene (from Step P2) (10g, 0.985 mol) in dry THF was added dropwise at -5 to 0°C followed by the addition of tatrakis (triphenylphosphine) palladium(O) (1.62g 1.40 mmol). The mixture was stirred at room temperature overnight (glc analysis revealed complete reaction). The mixture was then poured into 10% hydrochloric acid and the product was extracted into ether (twice) and the combined ether extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel: petroleum fraction (bp 40-60°C) - dichloromethane (10:1) to give colourless solid. Yield 4.18g (66%) mp 97-98°C.

6-butoxynaphth-2-ylethyne was prepared by an analogousmethod. Yield 82% mp 35-36°C. By a similar procedure compounds in which R^1 was alkyl were prepared.

Example 2 - Preparation of Type 1D Compounds



Step D1

A solution of 1-bromobutane (45g 0.33 mol) in acetone 100 ml was added dropwise to a stirred refluxing mixture of para-iodophenol (44g, 0.20 mol) and potassium carbonate (56g, 0.41 mol) in acetone (1L). The stirred mixture was heated under reflux for 24 hours (glc showed complete reaction. The potassium carbonate was filtered off, water was added to the filtrate and the product was extracted into ether (twice). The combined ethereal extracts were washed with water, 5% solium hydroxide, water and dried (Mg SO_4). The solvent and the excess of 1-bromobutane were removed in vacuo and the crude product was distilled.

Step D2

The procedure was the same as Route A, using lithium acetylide ethylenediamine complex (21g, 0.228 mol), zinc chloride (31.1g, 0.23 mol), the product of Step D1 (24g, 0.087 mol) and TTTP (3.17g, 0.27 mol). The crude product was filtered through a short alumina column to remove some of the TTPP and then distilled.

Step D4

1-iodo-4-pentyl benzene was prepared using a conventional diazotisation reaction followed by reaction with potassium iodide. Parapentylaninobenzene (20g, 0.12 mol), 36% hydrochloric acid (110 mol) sodium nitrite (10.50g, 0.15 mol) potassium iodide (43.5g, 0.26 mol). After steam distillation and work up the crude product was

distilled. Yield 29,00g (88%) bp 90-98°C at 0.1 mm Hg.

Step D4

The experimental procedure was as for Step D2. Lithium acetylide ethylene diamine complex (20.25g, 0.22 mol), zinc chloride (30.00g, 0.22 mol) product of Step D3 (3.12g, 2.7 mmol). Yield 7.89g (52%).

Step D5

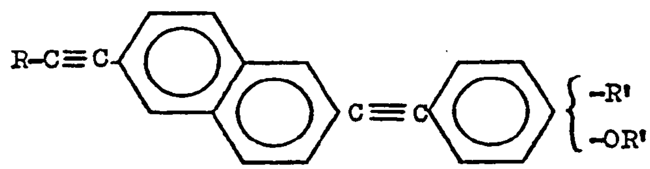
A solution of n- butyllithium (2.60 ml, 2.5M in hexane, 6.50 mmol) was added dropwise to a stirred, cooled (-5 to 0°C) solution of para-n-butoxyphenylethyne from Step D2 (1.10g, 6.32 mmol) in dry THF (50 ml) under dry nitrogen. This mixture was stirred for 10 minutes and then a solution of dry zinc chloride (0.90g, 6.62 mmol) in dry THF (100 ml) was added dropwise at -5 to 0°C. The mixture was stirred at room temperature for 15 minutes and a solution of 2-iodo-6-butoxynapthalene (from P2) (2.0g, 6.13 mmol) in dry THF (100 ml) was added dropwise at -5 to 0°C followed by the addition of TTPP (0.3721g, 0.32 mmol). The mixture was stirred at room temperature overnight and poured into 10% hydrochloric acid. The product was extracted into ether (twice) and the combined ether extracts were washed with aqueous sodium hydrogen carbonate and dried (Mg SO_4). The solvent was removed in valuo. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) dichloromethane 4:1) to give a colourless solid which was recrystallised from ethanol-ethyl acetate (20:1) to yield colourless crystals. Note: glc analysis revealed some of the starting naphthalene which was isolated during purification as a colourless solid. Yield 0.22g (22%).

By a similar procedure the corresponding compound where R(O) is butoxy and (O)R^1 is pentyl was prepared. Yield 64%.

Similarly the compounds where R(O) is methoxy and (O)R^1 is butoxy (Yield 64%) and where R(O) is and (O)R^1 are both butoxy and the phenyl ring is fluorinated in the 3-position (Yield 49%) were

prepared. In these 2 cases the reaction mixture was heated under reflux (100°C) for 22 hours after addition of the TTTP.

Example 3 - Preparation of Type IE Compounds



Step E1

A solution of boron tribomide (10.0ml, 22.0g, 0.088 mol) in dry dichloromethane (100 ml) was added dropwise to a stirred, cooled (-78°C) solution of 2-iodo-6-methoxynapthalene (Step P2) (10.0g, 0.035 mol) in dry dichloromethane (250 ml) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight (glc revealed a complete reaction). Water was carefully added and a yellow precipitate was produced. The product was extracted into ether (twice). The solvent was removed in vacuo. Yield 9.45g (100 %) mp 129-131.

Step E2

A solution of NPTFMS (8.35g, 0.023 mol) in dry dichloromethane (50 ml) was added dropwise to a stirred, cooled (-78°C) solution of the product of Step E1 (6.00g, 0.022 mol) and dry triethylamine (4.90g, 0.049 mol) in dry dichloromethane (80 ml). The stirred mixture was allowed to warm to room temperature overnight (glc and tlc - complete reaction). The mixture was washed with aqueous sodium carbonate and the separated aqueous layer was washed with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel/dichloromethane) to give a fawn solid. Yield 8.80g (100%) mp 65-66°C .

Step E3

The procedure was as for Route D above using pent-1-yne (1.60g, 0.0235 mol), the product of Step E2 (8.20g, 0.02 mol), TTPP (1.20g, 1.0 mmol) n-butyl lithium (2.35 ml, 10.0M in hexane 0.0235 mol) zinc chloride (3.20g, 0.0235 mol).

The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C)-dichloromethane) to give a pale yellow oil. Yield 6.33g (92%).

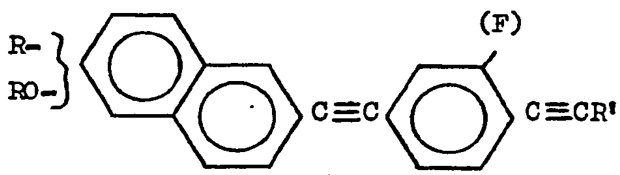
Step E4

A solution of n-butyllithium (3.95 ml, 2.6M in hexane, 6.33 mmol) was added dropwise to a stirred, cooled (-5 to 0°C) solution 1-parabutoxy-phenyl ethyne (1.10g, 6.32 mmol)$_2$ in dry THF (50 ml) under dry nitrogen. This mixture was stirred for 10 minutes and then a solution of dry zinc chloride (0.90g, 6.61 mmol) in dry THF (100 ml) was added dropwise at -5 to 0°C. The mixture was stirred at room temperature for 15 minutes and a solution of the product of Step E3 (2.05g, 6.00 mmol) was added dropwise at -5 to 0°C followed by the addition of TTTP (2.31g, 2.0 mmol) and lithium chloride (0.5810g, 0.014 mol). The mixture was then heated under reflux (oil bath 200°C) overnight (glc, tlc revealed complete reaction).

The crude product was purified by column chroma-tography (silica gel/petroleum fraction (bp 40-60°C)-dichloromethane 4:1 to give a colourless solid which was recrystallised from ethanol-ethyl acetate (1:1) to yield colourless crystals. Yield 1.41g (64%).

This procedure was repeated using 1-parapentoxyphenyl ethyne to prepare the analagous R^1 = pentyl compound. Yield 63%.

Example 4 - Preparation of Type 1G Compounds



Step G1

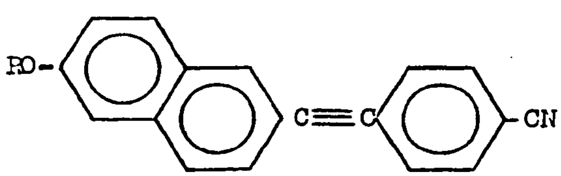
The procedure was as for Route D above, using pent-1-yne (5.28g, 0.078 mol) n-butyllithium (7.80 ml, 10.0M in hexane 0.089 mol), zinc chloride (10.80g, 0.079 mol), para-iodobromo benzene (5.28g, 0.78 mol), TTTP (2.80g, 2.40 mmol). Yield 14.2g (92%) bp 130-134°C at 15 mm Hg.

Step G2

The procedure was as for Step E4 using 6-butoxynaphth-2-ylethyne (Route A) (1.60g, 7.14 mmol), n-butyllithium (2.90 ml, 2.5M in hexane, 7.25 mmol), zinc chloride (1.00g, 7.35 mmol), the product of Step G1 (1-57g, 7.04 mmol) and TTPP (0.04129g, 0.36 mmol). The crude product was purified by column chromatography (silica gel/ petroleum fraction (bp 40-60°C)-dichloromethane 4:1) to yield a colourless solid which was recrystallised from ethanol-ethyl acetate (1:1) to yield colourless crystals. Yield 7.77g (77%).

By a similar procedure, starting from 1-fluoro-4-bromo iodobenzene the analogous fluorinated compound was prepared. Yield 49%.

Example 5 - Preparation of type IH Compounds



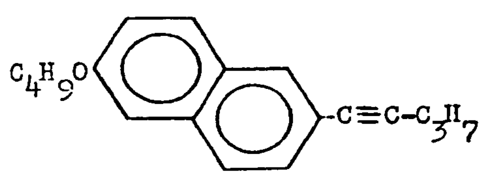
A solution of n-butyllithium (8.50 ml 2.5M in hexane, 0.021 mol) was add d dropwise to a stirred, cooled (-5 to 0°C) solution of the product of Route A(RO = methoxy) (3.86g, 0.021 mol) in dry

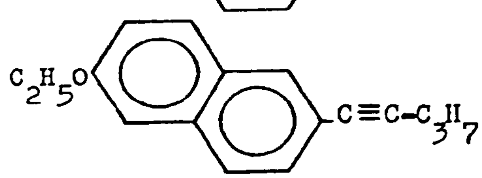
THF (50 ml) under dry nitrogen. The mixture was stirred for 10 minutes then a solution of dry zinc chloride (2.86g, 0.021 mol) in dry THF (100 ml) was added dropwise at -5 to 0°C. The mixture was stirred at room temperature for 15 minutes and a solution of para-bromobenzonitrile (3.86g, 0.021 mmol) in dry THF was added dropwise at -5 to 0°C followed by the addition of TTPP (0.97g, 0.84 mmol).

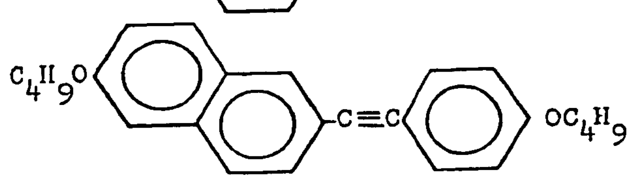
The mixture was heated at 50°C for 18 hours (glc, tlc showed complete reaction). The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) - dichloromethane 1:1) to give a pale yellow solid. <u>Yield</u> 4.68g (79%), a small quantity (0.50g) was recrystallised from ethanol-ethyl acetate (10:1) to yield colourless fluorescent crystals (0.30g).

Using an analogous procedure the corresponding butoxy compound was prepared. <u>Yield</u> 57%.

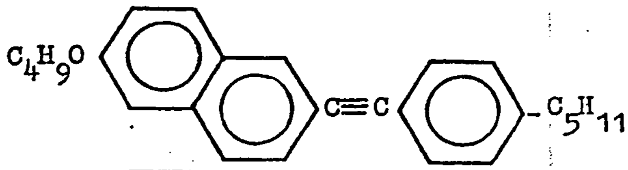
<u>Properties of Compounds Prepared in Examples 1-5 above</u>.
Liquid crystal transition temperatures (°C) for these compounds are listed below. K = solid crystal, N = nematic, I = isotropic liquid, S = smectic. ( ) indicates a virtual transition shown only on supercooling.

IA1  K 51 (N -23) I

IA2  K 65 (N -30) I

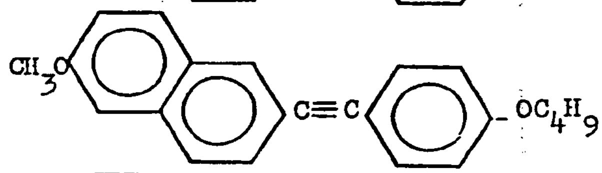
ID1  K 149 N 178.5 I

ID2



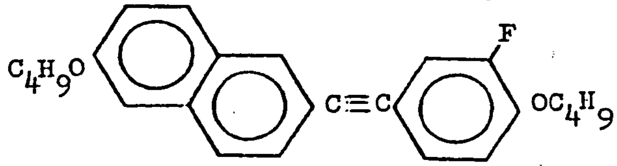
K 82 N 143 I

ID3



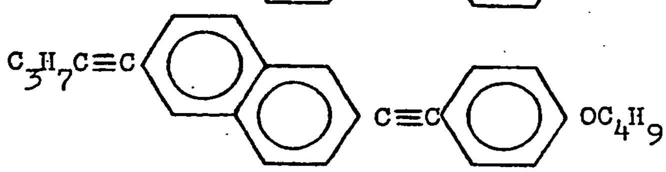
K 131 N 185 I

ID4



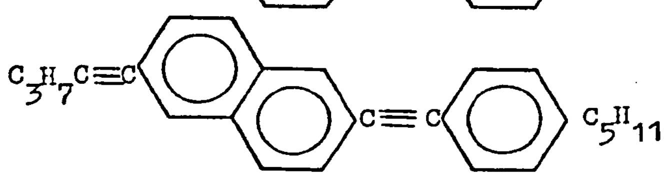
K 132 N 153 I

IE1



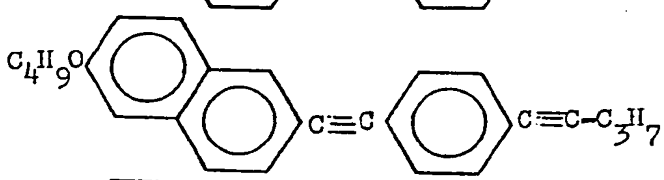
K 124 N 172 I

IE2



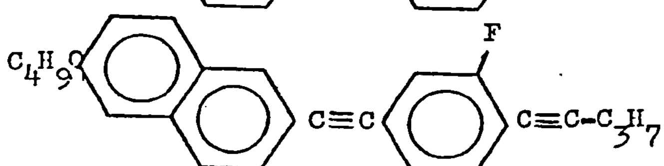
K 106.5 N 129 I

IG1



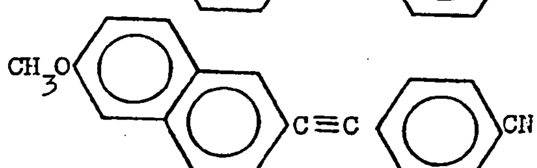
K 126.5 N 171 I

IG2



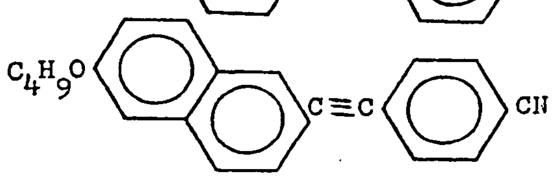
K 102.5 S_A 108.5 N 144 I

IH1



K 144 N 210 I

IH2



K 106.5 N 186 I

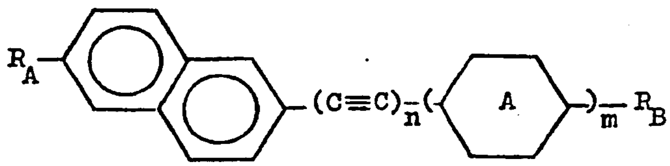
The birefringence Δn of some of these compounds in a ternery eutectic mixture of liquid crystalline compounds of formula VB above was measured:

Compound	Δn
IA1	0.24
IA2	0.25
IG1	0.45
IH2	0.42

These values for Δn compare favourably with the Δn value of the widely used liquid crystalline compound 1-pentyl-4^1-cyanobiphenyl which showed Δn = 0.24 in the same liquid crystal solvent. These results demonstrate that the naphthyl compounds of this invention are useful constituents of liquid crystal materials intended for uses where a high birefringence is required.

CLAIMS

1. Naphthyl compounds of Formula I



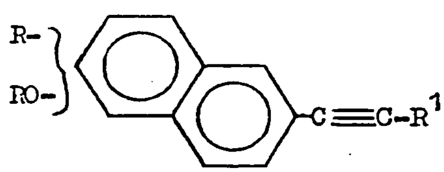
Formula I

wherein R_A is independently selected from R, RO, R-C≡C-

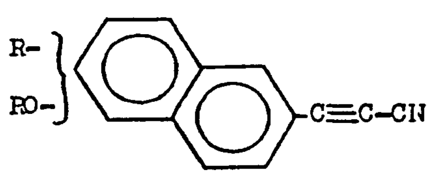
wherein R is C_{1-12} alkyl or perfluoroalkyl, wherein n is 0 or 1, m is 0 or 1, wherein ring A is phenyl, monofluorophenyl, difluoro phenyl or <u>trans</u> cyclohexyl; and wherein R_B is indepently selected from R^1, OR^1, $-C\equiv CR^1$, -CN or C≡C-CN where R^1 is C_{1-12}alkyl or perfluoro-alkyl, <u>provided</u> that the compound of Formula I contains at least one C≡C group and further provided that if n is 1 and m is 0 then R_B is not OR^1, $C\equiv CR^1$ or C≡CCN.

2. Napthyl compounds according to claim 1 wherein R and R^1 are straight chain alkyl.

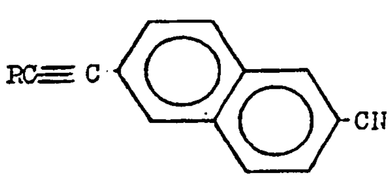
3. Napthyl compounds according to claim 2 having a Formula IA



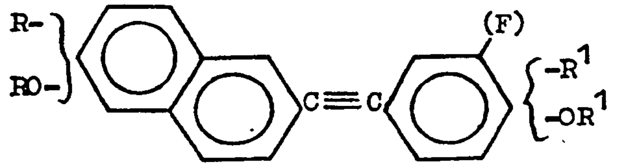
4. Napthyl compounds according to claim 2 having a formula IB



5. Napthyl compounds according to claim 2 having a formula IC

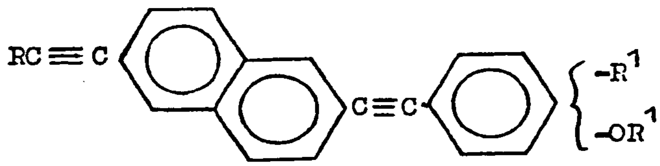


6. Napthyl compounds according to claim 2 having a formula ID

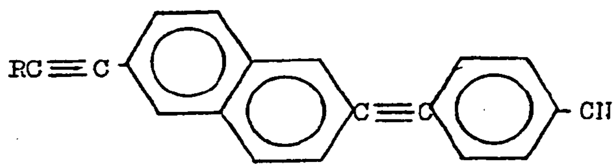


wherein (F) indicates that a fluorine substituent may be present on the indicated ring position.

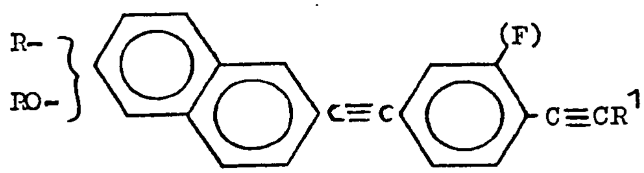
7. Napthyl compounds according to claim 2 having a formula IE



8. Napthyl compounds according to claim 2 having a formula IF

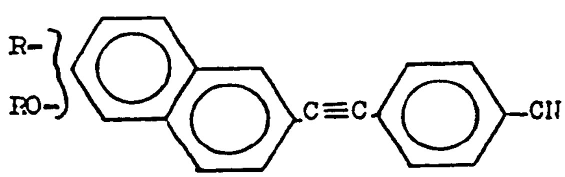


9. Napthyl compounds according to claim 2 having a formula IG



wherein (F) indicates that a fluorine substituent may be present on the indicated ring position.

10. Napthyl compounds according to claim 2 having a formula IH



11. Liquid crystal material, being a mixture of compounds which shows a liquid crystal phase, at least one of the compounds being a compound of Formula 1.

12. Liquid crystal material according to Claim 11 which shows a nematic liquid crystal phase.

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